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A New Method for Composition Control in Electroplating with Brass

A NEW METHOD FOR COMPOSITION CONTROL IN ELECTROPLATING WITH BRASS

BY

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THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

1920

UNIVERSITY OF ILLINOIS

May 25, 1920. 191

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

John Wesley Ziegler

ENTITLED A New Method of Composition Control in Electro-

plating with Brass.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemical Engineering.

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I

INTRODUCTION

1. Statement of the Problem.

Since the earliest days of the electroplating industry, the simultaneous deposition of two metals as an alloy has been of interest. Probably the alloy of greatest importance in this connection has been brass. Today it is deposited in industry from a cyanide bath, in many ways unsatisfactory. The object of this research was to study brass plating from cyanide baths, and methods of composition control, and to carry these principles of control to other baths, less expensive, less poisonous, and less liable to decomposition.

2. Historical - Review of the Literature.

In 1841, Elkington and Ruolz(1) discovered simultaneously yet individually, the use of cyanide baths in the plating of noble and base metals. At this time Ruolz intimated the possibility of depositing two metals simultaneously, while Elkington stated that alloys could be plated by depositing alternate layers and subjecting the plate to heat in a furnace. The deposit was to be protected while heating by being covered with carbon.

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1. Elkington and Ruolz: Comp. Rend. 13(1841) 998-1021.

On the basis of these reports, the Academy of Science referred further work on deposition of alloys to Ruolz. The report (1) of this continued work contained what Ruolz considered to be necessary conditions for the simultaneous deposition of two metals.

1. The solutions of each metal must not react to form objectionable compounds.
2. Observation of Faraday's laws that equal amounts of current do not deposit equal amounts of metals, but in proportion to their atomic(equivalent) weights.

There are many other conditions necessary, as anyone familiar with the subject can readily see.

Further work (2) along these lines was reported in 1848, in which several various and complex formulas were given. None of the work was satisfactory, because no control over the composition of brass was possible, chiefly because the solutions did not retain their several concentrations for the reason that the metals were used in different proportions from what they had in the initial solution.

Today brass plating is done entirely from cyanide solutions, a mixture of potassium copper and potassium zinc cyanides with a small excess of potassium cyanide, or with the potassium replaced by sodium. It is not satisfactory. Discoloration is very likely to occur, there is little range of composition

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1. Elkington and Ruolz. Comp. Rend. 15(1842) 466.
2. Chem. Zentrallblatt (1848) 506-508

control, the process is extremely slow, the cyanide is expensive and very poisonous. Therefore as early as early as 1848 (1) a departure from the use of cyanide was attempted. A solution, not containing cyanide was invented by Brunel, Bisson and Gangain. It was of no value, however, as copper only was deposited from the solution.

DeKay Thompson(2) in his work, "On the Simultaneous Electrolytic Deposition of Copper and Zinc from Various Solutions not Containing Cyanide" refers to and comments on the work of Charles B. Jacobs(3) to this effect.

Sulfate solutions of copper and zinc with rotating cathode and anodes of copper and zinc on opposite sides of the cathode were used. A high E.M.F. from one dynamo was applied between the zinc and the cathode, and a low E.M.F. from another dynamo between the copper and the cathode. The return wire is common to both dynamos. Thompson says that it is difficult to see how the arrangement would work, Since in the sulfate solutions of equal concentrations, the potentials of zinc and copper are over a volt apart and this difference cannot be reduced much by making the zinc ion concentration high and the copper low. If the current density is increased with the idea of reaching the potential difference between solution and cathode at which zinc would be deposited, copper is certain to come down in a spongy form.

1. Chem. Zentrallblatte (1848) 506-508
2. De Kay Thompson - Chem. and Met. Eng.(1912)-10-458
3. Charles B. Jacobs - Jour. Am. Chem. Soc. <u>27</u> (1905) 972-76

[illegible]

This comment is entirely in accord with the work of the author up to date.

The first method of controlling the composition of cyanide deposition was invented in 1858 by S. J. Goode(1). The current through the anodes was controlled by changing the depth to which the anodes were immersed or their distances from the cathode.

Here the idea came to De Kay Thompson(2) to make an attempt to get away from the cyanide electroplating baths entirely and to investigate whether some other electrolyte would in itself equalize the potentials of the two metals. The bath must not be too dilute for a good deposit, yet in order to have two metals deposit simultaneously, though their electrolytic pressures vary greatly, the less positive metal should be reduced so that the two potentials are nearly equal, i.e.

$$\frac{RT}{n_1 F} \log \frac{P_1}{p_1} = \frac{RT}{n_2 F} \log \frac{P_2}{p_2}$$

where the subscripts refer to the metals and the other letters have their usual significance. The equation is derived from the Nernst equation.

$$E = E_0 + 2.3 \frac{RT}{nF} \log \frac{C}{C_0}$$

simply by the elimination of constants.

It is not necessary to have exact equality, for the potentials are reduced, if an alloy is formed at the instant of deposition.

1. S. J. Goode. Chem. Zentrallblätte (1858) 350
2. De Kay Thompson, Met. and Chem. Eng. (1912) 10, 458

In addition the concentration change at the anode while current is passing increases(1) the potential difference between the cathode and solution. Believing that the only way of reducing to any extent the concentration of a large amount of metal in solution is by the formation of complex salts, Thompson studied all electrolytes where copper forms a complex ion with the idea that zinc does not form some of the complexes that copper does and also that the potential of the copper might be depressed more than that of the zinc, if the latter did form a complex.

His results briefly stated are:

1. Glycerine - Deposits appeared to be all copper.
2. Sugar - No evidence of zinc
3. Tartaric acid - No evidence of zinc
4. Glycocoll - No results because zinc also forms the glycocollate

$$Zn(NH_2CH_2COO)_2H_2O$$

5. Sodium potassium tartarate - This gave the first evidence of having zinc present. A solution of copper was made according to Brown and Mathers(2) containing in 1000 grams of water.

   60 g. $CuSO_4$ (.24 gram atom of Cu)

   50 g. NaOH

   159 g. sodium potassium tartrate

   A zinc solution was made containing in 1000 gram water

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1. Spitzer, Zeit. f. Elektroch. XI (1905) 345-68

2. Brown and Mathers Journ. Phys. Chem. X (1906) 39-51

.24 gram atom of Zn

140 grams NaOH

Equal volumes were mixed and the resulting bath electrolyzed with a current density of .3 ampere per square decimeter. Deposit was smooth, adhered well, and had a rich bronze color. Qualitative analysis showed presence of zinc. There was however, no composition control and the composition of the bath soon changed.

6. Thiosulphate - Gave fair percentage of zinc, but deposit was in the form of brown flakes and was found to contain sulphur.
7. Phosphorous acid - Only copper was obtained.
8. Ammonia - Though said to be all right by Morgan(1) it did not give any zinc.
9. Thioglycollate - Only copper deposited
10. Oxalate - Zinc sometimes present in product but results cannot be depended upon
11. Pyrophosphate - Though very promising at first, it gave results of no value.

Of the eleven complex salts thus tried, only four gave any zinc at all; the sodium potassium tartrate, the oxalate, the thiosulphate, and the pyrophosphate. Of these four complexes, the tartrate was the only one giving a smooth bright deposit for

1. J. L. R. Morgan. Jour. Am. Chem. Soc. XXII(1900) 93-99

any length of time. And though the tartrate gave a bronze color, the composition of the brass could not be depended upon.

In 1911, George Hogaboom(1), then secretary of the National Electroplater's Association, sent out over a hundred requests for unsolved problems in electroplating. Over eighty percent. of the replies were for an acid and brass solution and the elimination of the use of cyanide. Everything points to the problem as one worthy of attention and study, for which reason the author determined to investigate the problem with the hope that new information might be added to that already known.

II

THEORETICAL

1. Theory Used by Former Workers.

Former investigators have worked along two general lines, as one finds by studying the literature. As stated before, cyanide brings the potentials of copper and zinc close enough together that a brass will result by electrolyzing the bath. This is an example of the first theory, that the potential of the two metals must be equalized by the forming of complex salts so that both metals will deposit from the solution with equal ease. An anode of the composition to be plated is used.

The objections to this theory is that the composition of the bath changes because of poor corrosion of the anode. This results in a different percentage of the metals going into the solution

1. Hogaboom - Trans. Am. Electrochem. Soc. XIX(1911) 53-56

than the percentage contained in the anode. In addition it is quite difficult to get a complex salt that will adjust satisfactorily the potentials of the metals, so that a desired composition may be obtained in the alloy deposited. The cyanide bath is the only one that will give complexes of copper and zinc, that will allow a brass deposition. This allows but little control, and in addition the use of cyanides is objectionable in many ways.

The second theory is that by the use of two anodes, and by a high current density being forced through the anode of the metal least easily deposited, the deposition of that metal is forced along with the other.

The objection here is that the metal most easily deposited is thrown down in a spongy state because of the high E. M. F. imposed.

2. Theory Based on Faraday's Law.

It has been noted that in every case where a mixed electrolyte of copper and zinc has been used, except in the case of cyanide, that no zinc or only a mere trace is plated out. It was at this point that the thought came to the writer that in some way the electrolyte might be impoverished of copper content, controlled accurately by some device. If enough current passes to deposit a quantity of metal and there is not sufficient copper content to utilize all of that current, then zinc must deposit along with the copper. Therefore the plan was to electrolyze the bath continuously, but to supply only enough copper

to fill the required percentage in the deposit, which would necessitate the zinc making up the deficit. Faraday's laws of electrolysis state that the quantity of chemical action (in our case, metal deposited) is directly proportional to the quantity of electricity passing through the electrolyte and to the equivalent weight of the metal deposited. Therefore in the case of depositing brass, the following relation must exist between the deposit and the quantity of electricity passing through the solution.

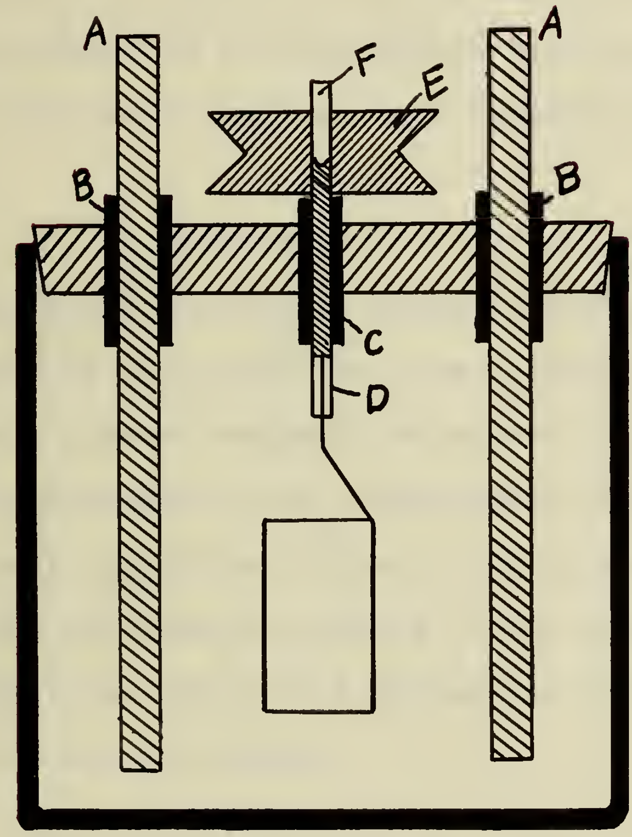
$$\text{Weight deposit} \times \left(\frac{\%\,Cu}{\text{Equiv. }Wt_{Cu}} + \frac{\%\,Zn}{\text{Equiv. }Wt_{Zn}} \right) = \text{Faraday's of electricity.}$$

III

EXPERIMENTAL

1. Apparatus.

   a. Electroplating Cell.

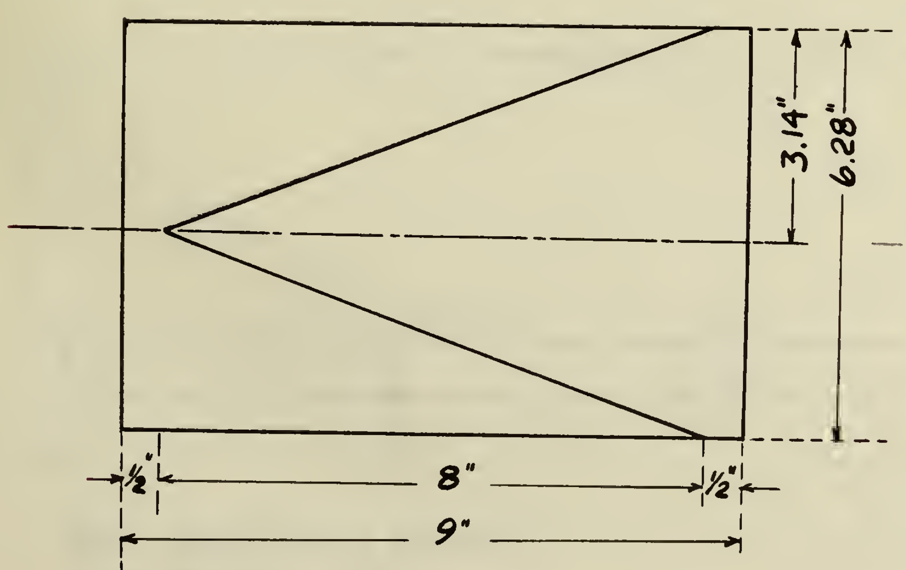


The experimental plating was carried cut in a cylindrical vessel four inches in diameter and about five inches in height. A cross section of the cell through the electrodes is given above. Two anodes AA, were used, one copper and the other zinc, which were placed opposite each other and on the diameter of the cylinder circle and supported in pieces of glass tubing BB passing through the cork used as a cover of the vessel. Through

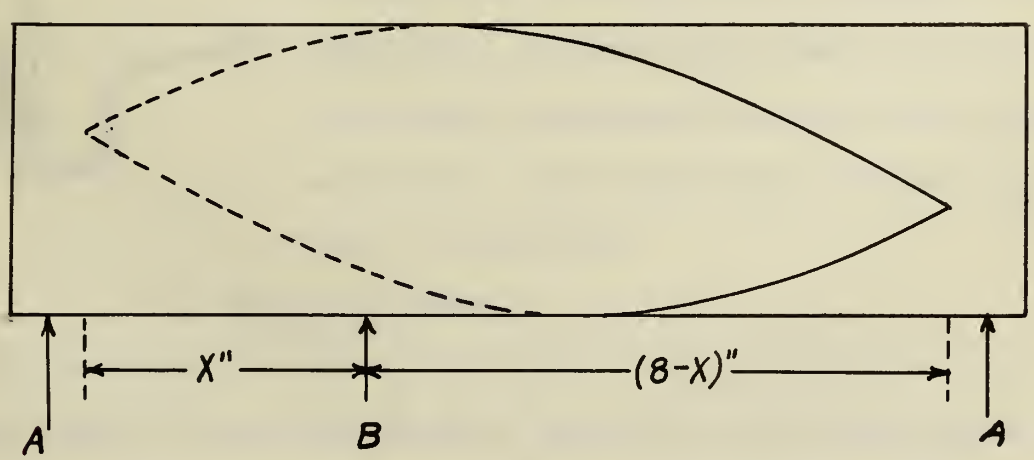
the center of the cork, a third piece of glass tubing C was located and this served as a bearing for the shaft D which gripped the cylindrical cathode of smooth platinum by means of an improvised chuck on the end of the shaft. The arrangement was rotated about seventy-five revolutions per minute by means of a pulley belted to a countershaft driven by a motor. Connection to the revolving shaft is made through a mercury pocket F at top.

b. Distributer.

For the purpose of controlling exactly the amount of copper and zinc passing into solution, the writer devised an instrument to distribute current between the anodes in any desired proportion. This distributer was a commutator form of instrument. A piece of brass tubing two inches in diameter and about nine inches long was cut into two pieces in the following manner. A piece of paper was cut to fit around the tubing exactly, and then laid out as per sketch.



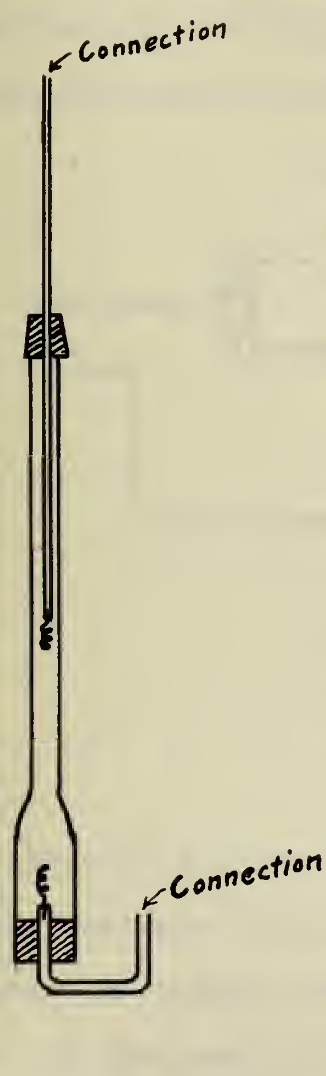
This diagram was fastened around the piece of tubing, which was marked along the lines by means of a prick punch, then cut by hacksaw. The result was two brass segments each resembling a quill pen. By means of brass ears soldered on the inside of the segments, they were mounted on fibre plates, which in turn were mounted on a steel shaft supported by ball bearings and driven by motor. The crevice between segments was filled with insulating cement. A copper brush was mounted at each end of the cylinder on fibre insulation, and bearing on the roller where the segment was continuous all of the way around. Another brush was mounted on a dove-tailed way; so that its position might be varied at will from one end of the instrument to the other. The positive current was led to this movable brush, and distributed between the two segments in the direct proportion that the position of the brush was from the respective ends. A sketch is shown giving an idea of the appearance of the roller segments and position of the brushes.



AA = Stationary Brushes
B = Movable Brush

c. Resistances.

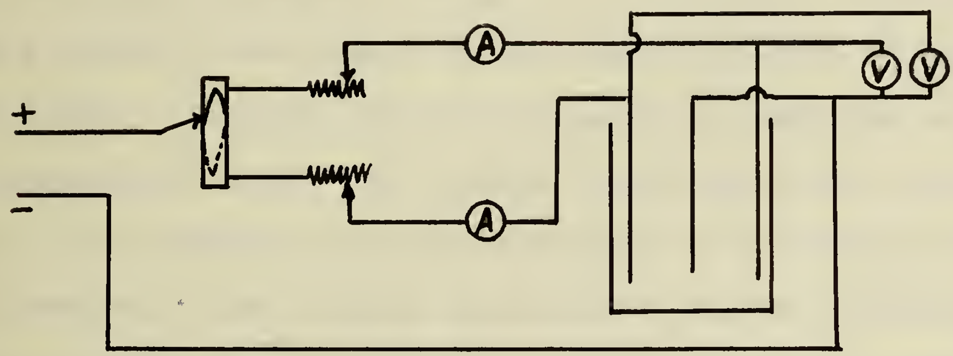
In order to be able to obtain the same current densities through both anodes, water rheostats were used. A small coiled wire platinum electrode was sealed into a U shaped piece of glass tubing. This was fitted into a stopper at large end of a condenser tube, which was mounted vertically with that end on the bottom. Another platinum electrode same as the above was sealed into a piece of glass tubing of small diameter and equal in length to the condenser tube. This was supported in the condenser tube by a stopper. Connections to the electrodes were made by mercury. It was necessary to use a capillary tube to fill the small tube. Water acidified with sulphuric acid is used as the electrolyte and variations of resistance are obtained by adjusting the distance between electrodes by moving the small tube through the stopper supported on top of the condenser tube. Very close and constant adjustment is obtained.



d. Wiring Diagram.

The positive current is led from the main switch to the movable brush on the distributer, where it is led alternately to one electrode and then the other. One stationary brush leads to

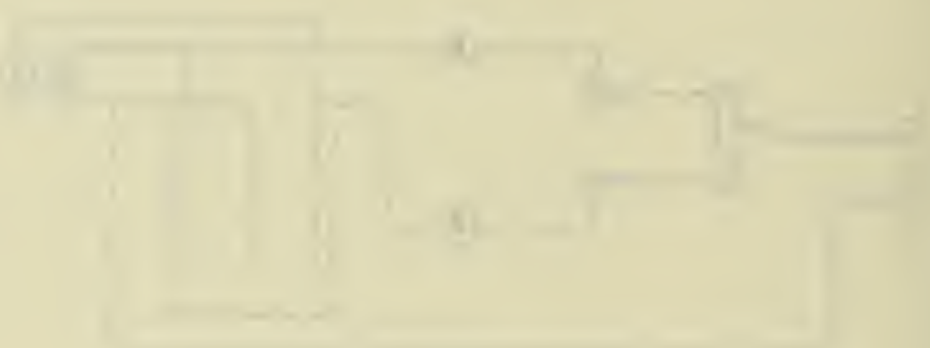
one rheostat and on through an ammeter to the copper anode, through the electroplating bath to the cathode and back to the negative side of the main line. The other stationary brush leads to a second rheostat, and through a second ammeter to the zinc anode, through the bath to the cathode and back to the negative side of the main line. Thus we have two individual circuits, which are alternately maintained.



A voltmeter is placed across the cathode and copper anode, and another between the cathode and the zinc anode. Voltaic action between the copper and zinc is prevented because only one circuit at a time is complete.

e. Electro Analysis Apparatus.

Apparatus ordinarily used in electro analysis was used. The solution to be analyzed was placed in a glass receptacle with a stopcock tube sealed in the bottom. A silver cathode



was supported in the solution and a platinum anode rotated within the silver cathode.

2. Manipulation.

a. Electrodeposition of the Brass.

Since zinc alloys with platinum upon deposition, the cathode was first cleaned, weighed, and electroplated with silver, as a prevention to platinum black forming. The cathode was weighed again, and the increase of weight is the silver. Then the cathode was placed in the chuck on the rotating shaft of the elctroplating cell. Several baths were used, but each was made up containing zinc alone. The movable brush upon the distributer was set in a certain position according to the composition of brass desired. The cathode was rotated and the resistance in the zinc circuit adjusted until a certain current passed through the bath. This was done while the movable brush rested on the segment of the distributer roll in the zinc circuit. The distributer was then turned until the movable brush rested on the segment in the copper circuit and the resistance adjusted until the same current was passing through the copper anode as was passing through the zinc anode just before. When the currents were balanced, the distributer was set in motion and revolved several hundred revolutions per minute. Since the same current passes through each anode, the amount of electricity through each is directly proportional to the distance of the movable brush from the base end of the commutator segment in series with that anode. After a deposit is made, the cathode is washed, dried,

and weighed. The increase in weight over the weight of the silver plated cathode is the weight of the brass.

b. Analysis.

In this work a very large number of analyses were necessary. The method which was used proved to be rapid and accurate. The complete deposit from the platinum cathode was dissolved off in nitric acid, diluted and just sufficient hydrochloric acid added to precipitate all of the silver. Precipitate was filtered and washed, and redissolved in the potassium silver cyanide solution to be used over and over in the plating of the platinum cathode. The washings were added to the brass solution. The excess acid was neutralized by ammonia after which 3 grams each of ammonium nitrate and urea were added and about five cubic centimeters of dilute nitric acid. The solution was brought to a volume of 125 c.c. and electrolyzed. The copper was deposited on a weighed silver cathode. After the deposition of copper was complete, the cathode was washed, dried, and weighed. The increase in weight gave copper content of the brass deposition, whose weight was determined by taking the difference between the weight of the silver plated platinum cathode and the weight of cathode after brass deposition. The zinc was determined by difference, which the author found entirely satisfactory, for this work.

IV

RESULTS

1. Cyanide Bath.

Zinc sulphate was dissolved in water and concentrated potassium cyanide solution added until the precipitate first formed was redissolved. About 500 c.c. of this solution was used as a bath. The movable brush on the distributer was placed about an inch from the zinc end of the distributer (that end from which current is led to the zinc anode). A series of good adherent deposits were made and analyzed. The first was chiefly a deposit of zinc, but contained a very small percentage of copper. Each successive deposit contained a higher percentage of copper until results were duplicated several times. Then the brush was moved farther from the zinc end of the distributer and another series of deposits made. Again successive deposits showed increases of copper percentage until several duplicate results were obtained. In this way a series of bright deposits, closely adherent, capable of taking a polish were obtained. In composition they ranged from a very small percentage of copper to a small percentage of zinc; and in color from a silvery luster with a peculiar copper glint to the reddish copper color of a high copper brass. The author had hoped to study the compositions in relation to the position of the movable brush on the commutator, but the time was too short. There are many factors entering into the relation which the author hopes to study at some future date. From work already accomplished nowever, he is confident that results may

[illegible]

be calculated in advance in this manner.

Copper exists in the cyanide solution as $KCu(CN)_2$ and zinc as $K_2Zn(CN)_4$. Thus copper has valence of one here, while zinc has a valence of two. Therefore the equivalent weight of copper in cyanide solution is equal to its atomic weight, 63.57; while that of zinc is one-half its atomic weight, or 32.68. Therefore to calculate the composition of brass in the case of 10% of the current passing through the copper anode, we apply these equivalent weights.

		Proportional weight of deposits
Copper	10 x 63.57	= 635.7
Zinc	90 x 32.68	= 2943.
Brass		= 3578.7

Percentage of Cu in brass is $\frac{635.7}{3578.7} = 17.78\%$, while that of zinc is 100-17.78 - 82.22%. The experimental value was found to be 17.12% for the copper, and 82.88% for zinc, which is quite close to the calculated value.

2. Sodium Potassium Tartarate Bath.

Encouraged by the success in controlling composition of brass plating in cyanide, the writer made up a zinc electrolyte with sodium potassium tartarate. In one liter was

60 g. $ZnSO_4$

140 g. NaOH

159 g. sodium potassium tartarate

From the bath deposits of brass varying in composition from a very small percentage of copper to high percentage, were obtained, while up to this time only small percentages of zinc could be

[illegible]

obtained in deposits from the sodium potassium tartarate bath(1) as seen in the introduction to this work. This bath was colorless at first but became blue as copper entered the electrolyte from the anode. As the copper percentages were increased in the deposits by moving the brush on the distributer toward the copper end, the solution became a deeper blue.

3. Oxalate Bath.

A bath was made up containing in one liter

5 g. oxalic acid
55 g. ammonium oxalate
15 g. zinc sulphate

The same type of results were obtained as in the sodium potassium tartarate solution.

4. Sulphate Bath

A bath was made up containing in one liter

200 g. zinc sulphate
40 g. sodium sulphate
10 g. zinc chloride
5 g. boric acid.

The results from this bath were discouraging, for as soon as any copper plated out, the deposit became spongy. However, the writer does not believe the bath is entirely useless, for it will probably work if some organic material is added to depress the ionization.

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1. De Kay Thompson - Chem. and Met. Eng.(1912)-10-458

V

DISCUSSION OF RESULTS

As was stated in the introduction, this problem was to study methods of control of brass composition, plated from cyanide baths and to apply those principles thus discovered to other baths. This was done, and brass was successfully deposited from other baths not containing cyanide, and made up of percentages of copper and zinc, controlled positively and accurately. Many side problems suggested themselves to the writer, who hopes to work them out sometime in the future. Some of these problems are:

1. The relative percentages of copper and zinc in the electrolyte and in the deposit.

2. The relative percentages of copper and zinc in the deposit and the quantities of current through the anodes. (Position of movable brush on the distributer.)

3. Current efficiences with various baths.

4. Best current densities to be used.

VI

CONCLUSION

1. That brass may be deposited from any electrolyte where the ionization is suppressed sufficiently to give a good firm adherent deposit, no matter how wide apart the electro-potentials of copper and zinc may be in the solution.

2. That by means of an accurate distribution of current to the two anodes, the composition of the bath will come to a point of equilibrium, where a definite composition in the deposition of brass is maintained.

3. That the composition can be varied at will by the changing of the distribution of current between the anodes.

4. That these principles are general and may be applied to any alloy.

VII

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ACKNOWLEDGMENT

The writer wishes to take this opportunity of expressing his gratitude to Dr. J. H. Reedy under whose supervision this work was accomplished, and to thank him for his encouragement and helpful suggestions, gladly given at all times.

John W. Ziegler.